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RELATIVISTIC EFFECTS ON THE EQUATION OF STATE OF THE LIGHT ACTINIDES

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Relativistic effects on the equation of state of the light actinides

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ABSTRACT

The effect of the relativistic spin-orbit (SO) interaction on the bonding in the early actinides has been investigated by means of electronic-structure calculations. Specifically, the equation of state (EOS) for the face-centered cubic (fcc) model systems of these metals have been calculated from the first-principles density-functional theory (DFT). Traditionally, the SO interaction in electronic-structure methods is implemented as a perturbation to the Hamiltonian that is solved for basis functions that explicitly do not depend on SO coupling. Here this approximation is shown to compare well with the fully relativistic Dirac treatment. It is further shown that SO coupling has a gradually increasing effect on the EOS as one proceeds through the actinides and the effect is diminished as density increases.

INTRODUCTION

The physics of the actinide metals is challenging both experimentally and theoretically. Recent progress in experimental techniques has, however, made it possible to study with greater detail the phase diagrams and EOS of these complex metals. This development of the experimental capabilities pushes theory to improve accuracy and explore the effects of various approximations in their implementations. Important steps in this direction, specifically valid for the actinides, were the inclusion of SO coupling [1], the usage of so-called full-potential (FP) techniques that could properly deal with distorted crystal structures [2], and the introduction of the generalized gradient approximation (GGA) [3,4].

A relativistic formulation of the theory usually begins with the Dirac equation. Within the formalism of the so-called atomic sphere approximation Brooks [1] and Söderlind *et al.* [5] showed that SO is important for the atomic density and bulk modulus for Np and Pu in particular. Andersen [6] proposed that instead of solving a four-spinor Dirac equation, one could include the largest relativistic effects in a Pauli equation where the smallest relativistic effect, the spin-orbit coupling, is introduced as a perturbation. Later, Nordström *et al.* [7] realized that the Andersen approach caused inaccuracies for the 6*p* band states which compromised the quality of calculations. One remedy for this, which seems to yield accurate results but has never formally been tested, is to simply omit the SO coupling on the 6*p* states [7,8].

In light of the need for accurate theoretical modeling of the actinides and the well known sensitivities of the theory to the treatment of the SO, we have chosen to investigate this issue in detail. We specifically investigate the SO effect (full Dirac, perturbation, or neglect) on the EOS. In order to isolate the dependence of SO coupling, we have chosen to focus only on the fcc crystal structure and not involve dependencies on the actual ground-state structures.

COMPUTATIONAL DETAILS

The electronic structure and total energy are obtained from two completely independent all-

electron methods. For the purpose of this investigation the significant difference is their implementation of the SO interaction. One method, the FP linear muffin-tin orbitals method (FPLMTO [9]), uses the Andersen approach [6] with the SO coupling excluded for the 6*p* states, unless otherwise stated. The "FP" refers to the use of non-spherical contributions to the electron charge density and potential. Here the basis functions are not dependent on the SO interaction. For the electron exchange and correlation energy functional, the GGA is adopted [3].

The other method, the exact muffin-tin orbitals method (EMTO [10]), solves the full Dirac equation [11] for which all relativistic effects are accounted for without approximation. The EMTO employs fully relativistic Green's function technique based on the improved screened Korringa-Kohn-Rostoker method. The calculations are performed for a basis set including valence *spdf* orbitals whereas the core states were recalculated at every step in the iteration. As in the case of the FPLMTO method, GGA [6] is used for the exchange/correlation approximation.

The EOS for the respective phase and metal is obtained from a fit of the total energies to a Murnaghan form [12]. Because there are substantial differences in various approximations between the FPLMTO and the EMTO methods, we are comparing the relative effect of spin-orbit coupling in the respective method. This way, the difference in the treatment of the object of interest is emphasized over other numerical approximations of the two methods.

RESULTS AND DISCUSSION

We focus on the EOS and its dependence on SO coupling and choose to present the results as the relative error in pressure, P_{error}, as a function of volume, associated with the neglect (noSO) of this effect, $P_{error} = \frac{P_{SO}(V) - P_{noSO}(V)}{P_{SO}(V)}$.

As V approaches the equilibrium (SO) volume, P_{SO} goes to zero and the relative error goes unbound, even though the absolute error might be small. For this reason we only plot the relative error for volumes somewhat smaller than V_0.

We mentioned in the introduction that the pertubative approach [6] to include SO coupling into the calculations causes inaccuracies [7] when the 6*p* states are considered as valence or semi-core states. This is the case for any actinide calculation, and in Fig. 1 we show the dramatic effect of this inaccuracy for Th. Clearly, the SO coupling on the 6*p* states gives rise to a considerable, artificial, distortion of the EOS.

In Fig. 2 we show P_{error} for Th as obtained from FPLMTO (dashed line) and EMTO (full line). For both methods the relative error is quite small, and for the FPLMTO, P_{SO} and P_{noSO} are numerically close to identical. For EMTO the relative error is only about 5 % at 10 % compression and vanishes completely at less than 20% compression. For the proceeding metal in Fig. 3, Pa, the error made by ignoring the SO effect is no longer negligible at ambient conditions. Nevertheless, both methods show that the SO effect on the EOS can safely be ignored at compressions beyond about 20% for Pa. Notice that the relative errors, as calculated by FPLMTO and EMTO, are quite similar. Apparently, the approximate SO formulation by Andersen [6] compares well with the exact treatment of the SO interaction within the EMTO method [11]. Next, we plot the same property for uranium in Fig. 4. Now the SO effect on the EOS is very obvious. For U, the relative error is substantial and only at significant compressions it approaches zero. Again, the FPLMTO and EMTO methods produce nearly identical results.

We have identified the following facts. (i) The effect of SO on the EOS is nearly negligible for Th but gradually increases as one proceeds from Th to U. (ii) Applied pressure always

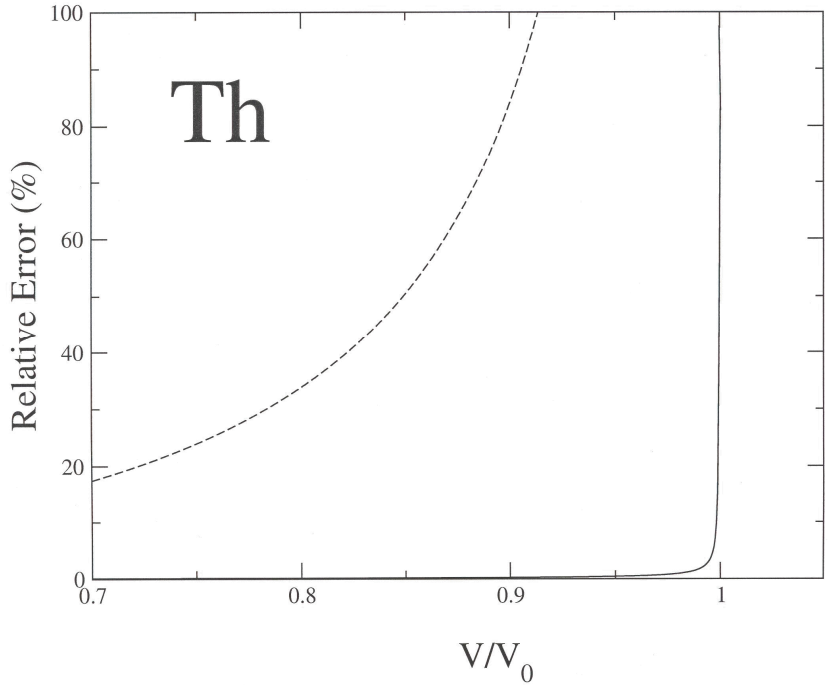

Figure 1. Relative pressure error for Th at two levels of approximation. Solid (dash) line refers to SO coupling for the semi-core 6*p* states excluding (including) within the pertubative fashion.

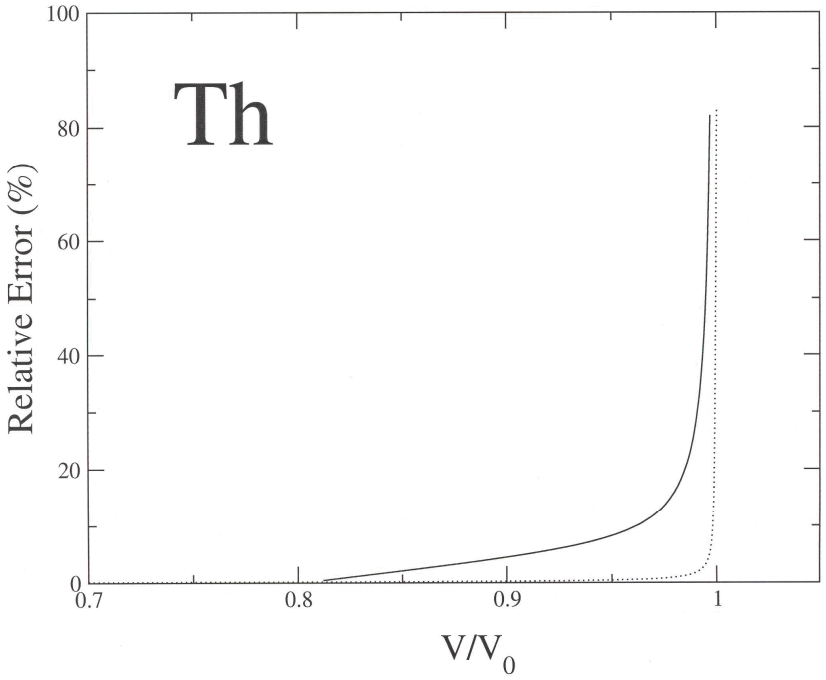

Figure 2. Relative pressure error for Th when neglecting SO coupling as a function of scaled volume (V/V_0) for EMTO (full line) and FPLMTO (dashed line).

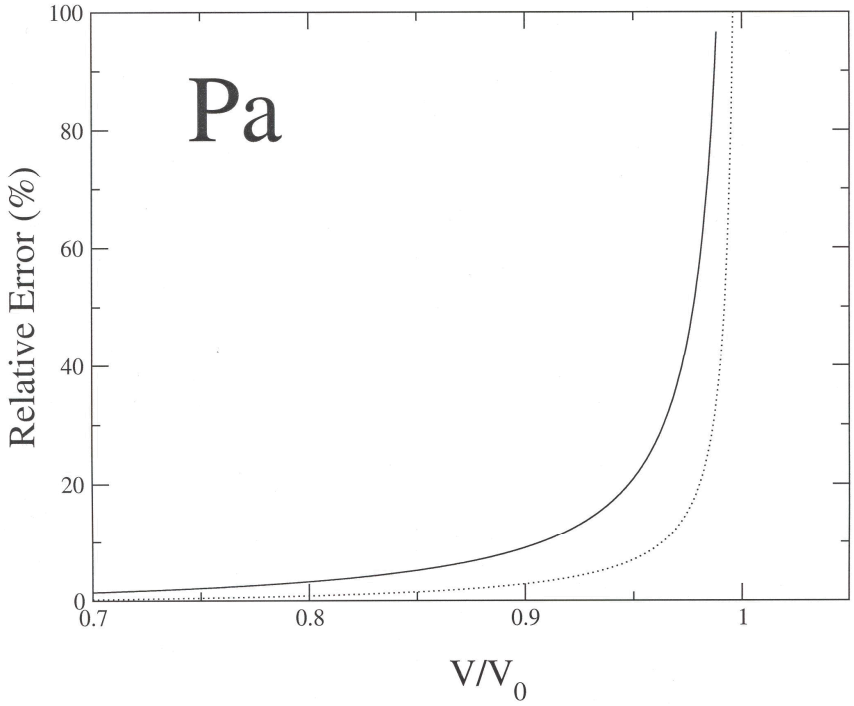

Figure 3. Relative pressure error for Pa when neglecting SO coupling as a function of scaled volume (V/V0) for EMTO (full line) and FPLMTO (dashed line).

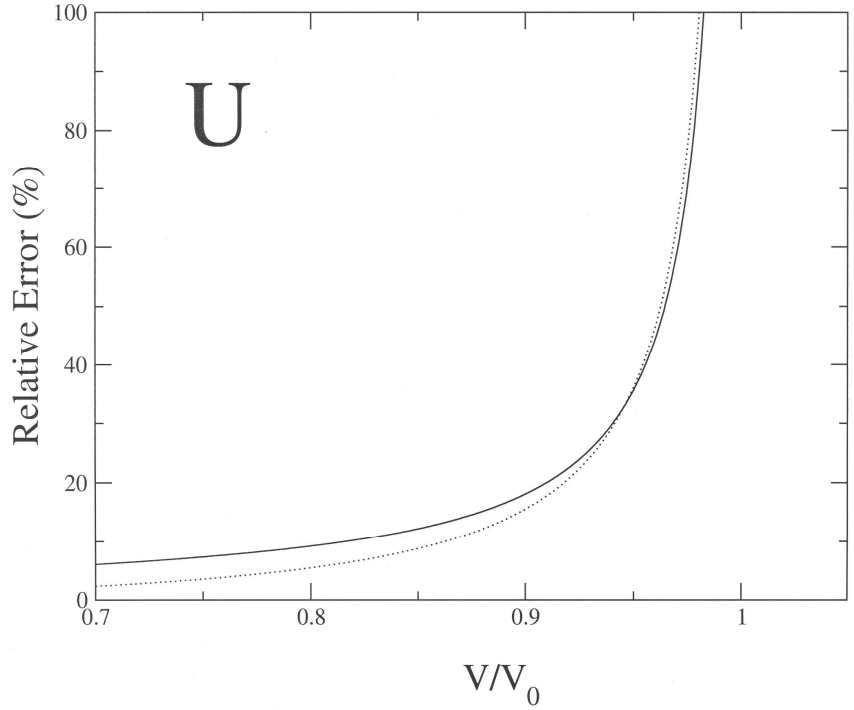

Figure 4. Relative pressure error for U when neglecting SO coupling as a function of scaled volume (V/V0) for EMTO (full line) and FPLMTO (dashed line).

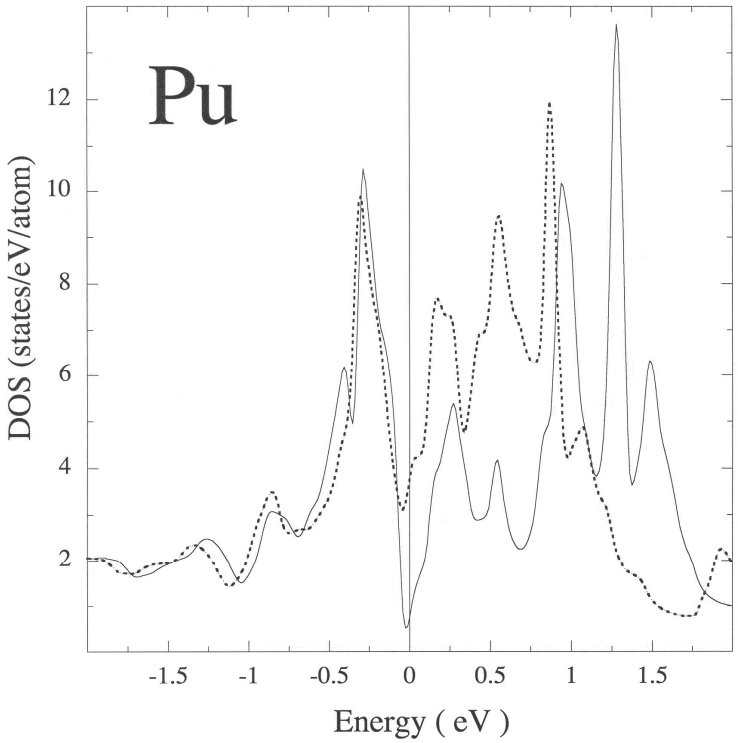

Figure 5. DOS for Pu at the equilibrium volume. The FPLMTO calculations include (full line) and exclude (dashed line) SO coupling. The Fermi energy is shifted to zero energy.

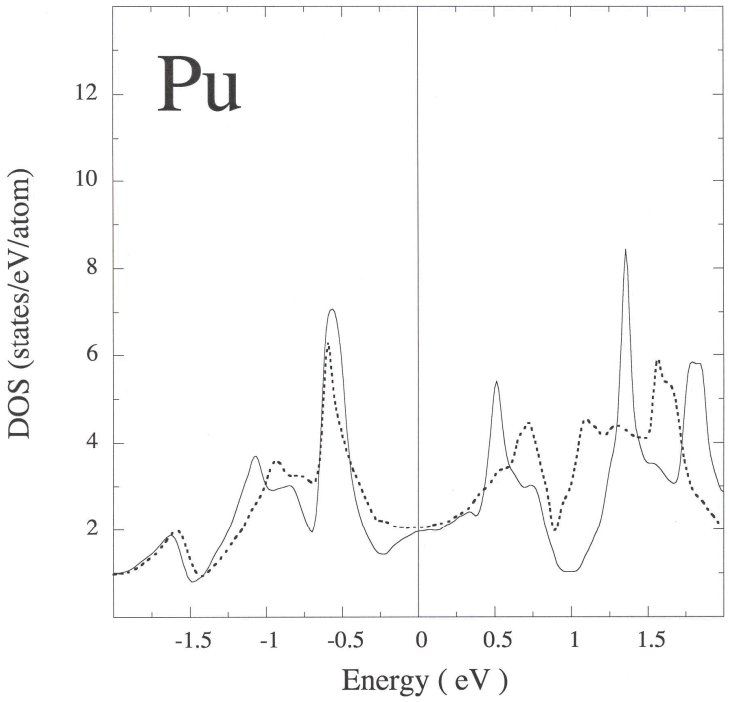

Figure 6. DOS for Pu at significant compression. The FPLMTO calculations include (full line) and exclude (dashed line) SO coupling. The Fermi energy is shifted to zero energy.

suppress the effect of SO coupling, although for U a significant compression is needed to fully deplete the effect.

One consequence of (i) is that the calculated equilibrium volume and bulk modulus depend on the inclusion of SO in the calculation, especially for Np and Pu, see the Table. The volumes increase and the bulk moduli decrease.

In order to explain the second point, (ii), we plot in Fig. 5 the DOS for Pu with (full line) and without (dashed line) SO coupling. Notice, that the DOS at the Fermi energy (zero) is greatly reduced as a consequence of the SO interaction. This will have a stabilizing effect and lower the total energy considerably. Next, we plot DOS again for Pu, but now at significant compression, see Fig. 6. The DOS at the Fermi level for both calculations is nearly the same. Hence, the compression has greatly diminished the SO effect on Pu.

Table. Equilibrium volumes ($Å^3$), and bulk moduli (kbar) for fcc Th-Pu as calculated by the EMTO method.

Element	Equilibrium volume		Bulk modulus	
	SO	noSO	SO	noSO
Th	33.0	32.8	536	641
Pa	26.2	25.9	1020	1040
U	23.1	22.7	1090	1130
Np	20.6	19.9	1520	1690
Pu	20.5	18.5	890	1790

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